CHALMERS
UNIVERSITY OF TECHNOLOGY

Specific ion effects in the adsorption of carboxymethyl cellulose on cellulose: The influence of industrially relevant divalent cations

Colloids and Surfaces A: Physicochemical and Engineering Aspects 626 (2021) 127006

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

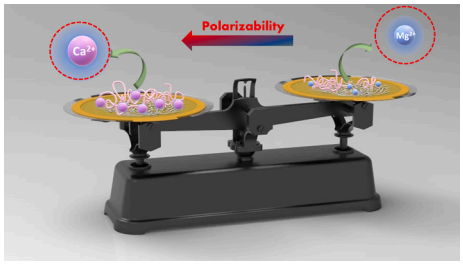
journal homepage: www.elsevier.com/locate/colsurfa

Specific ion effects in the adsorption of carboxymethyl cellulose on cellulose: The influence of industrially relevant divalent cations

Vishnu Arumughan [a,b], Tiina Nypelö [a,e], Merima Hasani [a,b], Harald Brelid [c], Sverker Albertsson [c], Lars Wågberg [d,f], Anette Larsson [a,b,e,g,*]

[a] Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden
[b] AvanCell, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden
[c] Södra Innovation, Väröbacka, Sweden
[d] Department of Fibre and Polymer Technology, Division of Fibre Technology, KTH Royal Institute of Technology, Teknikringen 56–58, Stockholm, Sweden
[e] Wallenberg Wood Science Center, Chalmers University of Technology, Gothenburg, Sweden
[f] Wallenberg Wood Science Center, KTH Royal Institute of Technology, Stockholm, Sweden
[g] FibRe – Centre for Lignocellulose-based Thermoplastics, Department of Chemistry and Chemical Engineering, Chalmers University of Technology, SE-412 96, Gothenburg, Sweden

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Specific ion effects
Polymer adsorption
Carboxymethyl cellulose
Adsorption to cellulose surfaces

ABSTRACT

The adsorption of carboxymethylcellulose (CMC) on cellulose surfaces is of relevance from both academic and industrial perspectives as it facilitates resource-efficient modification of cellulose fibres that allows them to carry negative charges. It is known that, compared to monovalent ions, Ca^{2+} ions are superior ions in facilitating CMC adsorption and the subsequent introduction of charge on cellulose fibres. However, the formation and deposition of calcium oxide involved in this process necessitates the search for alternative cations. Magnesium ions form one of the more promising candidates since they are already used in the pulping process to prevent cellulose degradation during peroxide bleaching. This work aims at elucidating the effects of the industrially relevant alkaline earth metal divalent cations Mg^{2+} and Ca^{2+} on the CMC adsorption process onto cellulose surfaces. Quartz Crystal Microbalance (QCM-D) technology was used to follow the adsorption in model systems in real time, whereas the adsorption of CMC on commercial fibres was studied using polyelectrolyte titrations, total organic carbon (TOC) analysis and conductometric titrations. This study shows that the presence of Ca^{2+} ions was more favourable for the adsorption of CMC to both types of cellulosic surfaces than Mg^{2+} ions. The distinction in the adsorption behaviour in the presence of Mg^{2+} and Ca^{2+} is suggested to be due to the differences

* Corresponding author at: Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg, Sweden.
E-mail address: anette.larsson@chalmers.se (A. Larsson).

https://doi.org/10.1016/j.colsurfa.2021.127006
Received 26 April 2021; Received in revised form 7 June 2021; Accepted 8 June 2021
Available online 11 June 2021

in the polarizability of the ions. The findings are decisive in designing efficient industrial processes for the adsorption of polyelectrolytes to cellulose surfaces of similar charge.

1. Introduction

The application of polyelectrolyte adsorption and Layer-by-Layer assembly at a solid-liquid interface is a flexible and versatile approach for surface modifications [16]. Cellulose-rich materials have been functionalized by cationic and anionic polyelectrolyte adsorption and, by the wise selection of polymers and other functional entities, it is possible to create interactive and reactive surface layers [42]. The interaction of cationic polyelectrolyte with negatively charged cellulose surface is attractive and is already utilized in the paper industry to improve the physical properties of paper products. Anionic polyelectrolytes such as carboxymethyl cellulose (CMC) can also be adsorbed on negatively-charged cellulose surfaces [27–29,4]. CMC is a negatively-charged water-soluble polyelectrolyte derived from cellulose [12,18,37]. It has a wide range of applications in pharmaceutical products, foods, mineral processing, paper making etc [27,28,45]. Especially in mineral processing and paper making adsorption of CMCs on surfaces are important.

The adsorption of anionic CMC on negatively-charged cellulosic surfaces has been theorized to arise from the electrostatic repulsion being overpowered by non-ionic attractions, despite the fact that electrostatic repulsion is to be expected [5,15]. Laine et al. proposed that the irreversible attachment of CMC onto cellulose is due to its co-crystallization on the cellulose surface since they have similar backbone structures [28]. The experimental evidence on this, however, remains ambiguous.

Kargl et al. investigated CMC adsorption on polymer films with varying degrees of cellulose character under different pH conditions [22]. Their results suggested involvement of a specific interaction between CMC and cellulose in the adsorption process, in agreement with a theory introduced by Scheutjens and Fleer (1995). However, Kargl et al. did not discuss the driving forces behind the adsorption to the cellulose surfaces [22].

As in many interfacial interactions and processes, the presence of salts has a profound effect on the adsorption of CMC on cellulosic surfaces, where the amount of adsorbed material increases as concentration of salt increases. Liu et al. [29] suggested that this is due to an entropically-driven ion-exchange process, whereby the monovalent cations around the CMC chain are replaced by the divalent cations mediating an electrostatic bridging between the CMC and the cellulosic surface. It has been demonstrated that divalent cations can introduce ion specificities in interfacial processes for highly charged polyelectrolyte brushes of PSS (polystyrene sulphonate) due to differences in the ionic radii, state of hydration and binding energies [44]. Thus far, however, in-depth knowledge of the specific ion effects in CMC adsorption on cellulose surfaces is lacking.

Traditionally, CMC has been used as a paper additive to improve the mechanical properties and processability of paper products either alone, or in combination with, for example, common wet strength agents [27]. CMC adsorption has been integrated in the papermaking process to modify fibres within the production line [10,26]. Integration of a polymer adsorption step within the process in paper mills is economically viable and abides by green chemistry principles. Nevertheless, there are certain issues that need to be resolved in order to design a well-optimized industrial process. One of the major challenges in integrating CMC adsorption is the utilisation of $CaCl_2$: its usage is undesirable in the Kraft pulping process due to the scaling problems caused by calcium oxide deposits in pipelines [14]. An industrially viable divalent cationic electrolyte system should therefore be used for modulating the adsorption of CMC on cellulose surfaces. One of the promising candidates for this purpose is the magnesium ion, since magnesium salts are already used in the oxygen delignification stage in Kraft pulping for preventing degradation and improving yields. Magnesium ions are also found to increase pulp brightness when used in hydrogen peroxide bleaching stages [8].

The aim of this work is to elucidate the effects of the industrially-relevant alkaline earth metal divalent cations Mg^{2+} and Ca^{2+} on the CMC adsorption process onto cellulose surfaces. A model system approach has been combined with traditional systematic adsorption studies on macroscopic cellulose-rich fibres, which can verify the applicability of model system studies to a real cellulosic macrofibre system. The findings contribute to facilitating a fouling-free and resource-efficient process of fibre modification being integrated into a papermaking process line.

2. Experimental

2.1. Materials

A never-dried Scandinavian softwood Kraft pulp from Södra Cell was used in the experiments with cellulose fibres. The pulp was industrially produced and had been bleached in an elemental chlorine-free (ECF) sequence, namely D(OP)D(PO), where D stands for a stage with the addition of chlorine dioxide, OP for an oxygen delignification stage and PO for a pressurized peroxide stage. This bleaching was performed until ISO Brightness 90% was reached. Cellulose nanofibres from softwood Kraft fibres were procured from Stora Enso, Stockholm. Magnesium chloride ($MgCl_2$), calcium chloride ($CaCl_2$), deuterium oxide and polyethyleneimine-branched polymers (with an average Mw of 25 kDa) were purchased from Sigma Aldrich.Carboxymethylcellulose (Blanose 7LPEP) with a molecular mass of 90.5 kDa and a degree of substitution (D.S.) of 0.7 (according to the supplier) was kindly provided by Ashland. Ultra-filtrated (Mw>500 kD) poly-DADMAC (Mw 550 kD) with a charge density of 6.2 meq/g was purchased from RISE, Stockholm, and polyethylene sodium sulphonate (Na-PES) from Paper Test Equipment AB, Sweden. All polymers were used as received.

2.2. Method

2.2.1. Preparation and characterization of ultra-thin cellulose model films for adsorption measurements

Thin cellulose model films were prepared using SiO_2 coated QCM-D sensors (supplied by Q-Sense AB, Gothenburg) as a base. These were spin-coated with a cellulose nanofibre suspension according to the protocol described in the Supporting Information. The morphological features and quality of cellulose model films were evaluated by atomic force microscopy (NTEGRA Prima setup NT-MDT Spectrum Instruments, Moscow) in semi-contact mode. The uniformity of the cellulose model films was investigated by scanning the height profile at three random spots in different locations on the films and observation of the root mean square roughness.

The water content of the CNF model films was determined by quartz crystal microbalance with dissipation monitoring (QCM-D) (Q-Sense AB, Gothenburg) using a D_2O-H_2O solvent exchange method [7,24]. In this procedure, the spin-coated QCM-D sensors were placed in the flow cell and deionized water was injected into the flow cell at the rate of 100 µl per min for 3 h to reach a plateau in the frequency. The solvent was then switched to D_2O and an immediate drop in frequency was observed, due to the relatively high density of D_2O. After 10 min, the solvent was switched again but this time to water, and the shift in frequency was recorded. The difference in the frequency changes for the bare sensor and the CNF-coated sensor during the H_2O - D_2O exchange was used for

the calculation of the water associated with the spin-coated CNF film.

2.2.2. Dynamic light-scattering experiment

The behaviour of CMC solutions in different electrolyte conditions was characterized using DLS. Samples for DLS experiments should be prepared with the utmost of care, so dust-free containers were used for preparing the CMC solution. A 0.02% (w/v) of CMC solution was prepared by dissolving CMC in Millipore filtered deionized water, with continuous overnight stirring to ensure complete dissolution. The concentration of electrolyte in the solution was adjusted by adding predissolved concentrated salt solutions (1 M). The samples were then centrifuged to remove any undissolved CMC components.

2.2.3. Adsorption experiments using QCM-D

The adsorption behaviour of carboxymethyl celluloses onto model cellulose nanofibre films was monitored using QCM-D and the specially prepared sensors with CNF. CMC solutions of concentration 0.02% (w/v) containing 20 mM of either $MgCl_2$ or $CaCl_2$ were injected into the flow cells. The frequency changes were registered at 5 MHz fundamental resonance frequency and its several overtones. A model introduced by Johannsmann et al. [21] was used to calculate the adsorbed mass: it is important to note that the sensed mass calculated using this model includes the mass of the CMC as well as the water that is associated with the adsorbed layer, and is thus not equal to the dry mass of CMC adsorbed.

2.2.4. Preparation of fibres for the adsorption studies

It has been shown earlier that fines from cellulose fibres adsorb much more polymers due to their higher specific surface area [41]. Fines were therefore removed according to the procedure described by Köhnke et al. [25] and the resulting cellulose fibres, devoid of fines, were ion-exchanged into their sodium form [25].

2.2.5. Adsorption of CMC on bleached softwood Kraft pulp fibres

Wet, pretreated, pulp fibres corresponding to 5 g dry material were dispersed in deionized water containing dissolved $CaCl_2$ or $MgCl_2$. After the addition of wet fibres, the concentration of the $CaCl_2$ or $MgCl_2$ in the water phase was 20 mM; the temperature of the fibre suspension was kept at 40 °C in a vibrating water bath. A CMC solution containing 20 mM salt ($CaCl_2$ or $MgCl_2$) was added into the fibre suspension and the pH of the suspension was adjusted to 7 using 0.01 M sodium hydroxide. The final consistency of the fibre suspension was 5% (w/w %). After 2 h, the suspension was filtered and washed with 750 ml of 20 mM corresponding salt solution; the 1st filtrate and the washed pulp were collected separately for further analyses. The control experiments were conducted under different salt environments without adding CMC but maintaining other conditions, such as consistency, pH and temperature, as previously.

2.2.6. Analysis of adsorption on pulp

2.2.6.1. Analysis of the content of total organic carbon (TOC) in the filtrate. The filtrates after adsorption were subjected to Total Organic Carbon (TOC) analysis according to SS-EN 1484 using a TOC 5050A Schimadzu instrument in order to estimate the amount of unabsorbed CMC present in the filtrate.

2.2.6.2. Analysis of the anionic charge of the filtrate by polyelectrolyte titration. The anionic charge of the filtrate was determined by titration of the filtrate obtained from the reference pulp and the CMC modified pulp under different salt environments. The pulps were filtered using a Büchner funnel fitted with a 100 μm nylon filter; 10 ml filtrate was titrated with 0.2 mM PolyDADMAC using a Mütek PCD 03 instrument (Germany).

2.2.6.3. Analysis of the total charge of the modified pulp by conductometric titration. The total charge of the reference pulp and the CMC modified pulp under different salt environments was also analyzed by conductometric titration. The modified pulp was protonated by treating it with 0.1 M HCl solution and the pH was adjusted to 2. The protonated pulp was washed thoroughly to remove the excess amount of acid before being titrated against 001 M NaOH using an automated conductometric titrator (Metrohm Conductivity Module 856, Sweden).

2.2.6.4. Analysis of the surface charge of modified pulp by polyelectrolyte titration. The surface charge of the starting pulp and the CMC modified pulp was analyzed by polyelectrolytic titration ([43], and further optimized by Horvath [19]). Prior to titration, the carboxylate groups in the pulp were ion-exchanged into their sodium form. First, 5 g of pulp was protonated by immersion in 0.01 HCl (0.5% pulp consistency) and adjusted to a pH of 2 with 0.1 M HCl solution. The pulp was then soaked for 30 min, dewatered with the aid of a Büchner funnel and, finally, rinsed with deionized water until the conductivity of the filtrate was below 5 μS/cm. The dewatered pulp was transferred to a beaker containing 1000 ml 1 mM $NaHCO_3$ and the resulting pulp suspension was agitated, before 0.1 M of NaOH was added until a stable pH of 9 was achieved. After 30 min, the pulp was again dewatered with the aid of a Büchner funnel and washed with deionized water until the conductivity of the filtrate was below 5 μS/cm.

Five portions of the pulp corresponding to approx. 0.5 g each (1/10 of the wet pulp in its sodium form) was added to a mixture of 75 ml deionized water and 5 ml 0.2 mM NaCl. Five levels of a polyDADMAC solution (0.5 g/l) were the added to the diluted pulp samples and the final volume of water in each sample was adjusted to 100 ml by addition of deionized water. The samples were then agitated for 30 min and after that, the pulp was dewatered with the aid of a Büchner funnel. The resulting pulp was dried and weighed in order to determine the actual amount of pulp in each sample and the filtrate was analyzed for non-adsorbed polyDADMAC by titration with 0.2 mM Na-PES using a Mütek PCD 03 instrument. The surface charge was then calculated from the adsorption isotherm.

3. Results and discussion

3.1. Characterization of ultra-thin cellulose model films

The AFM height profiles obtained for the nanofibrillated cellulose-coated QCM-D sensor (Fig. 1a) reveal the fibrillar features (fibre diameter range: 8–15 nm). The films had a root mean squared roughness (RMS) of 3.7 nm as calculated over an area of 1 μm × 1 μm, which is consistent with previous reports [2].

A D_2O-H_2O solvent exchange method, described in the literature [7, 24], was employed to acquire further information of the physical state of the CNF film. The difference observed in $\Delta f/n$ between the bare sensor and CNF film-coated sensor provides information of the solvent associated with the surface. The solvent fraction estimated in the film is considered to be an indirect measure of the void volume on the surface of the CNF model film [40]. Fig. 2 shows a representative D_2O-H_2O exchange curve of a bare SiO_2 surface and CNF film, where the latter was found to be associated with 39 mg m^{-2} of water. Both AFM and solvent exchange studies revealed that CNF film has a morphology that contributes to a large surface area being available for interaction with the solvent and the adsorbates.

3.2. Hydrodynamic size of CMC solutions determined by dynamic light scattering

Evaluation of the number distribution of the hydrodynamic size of CMC in 20 mM salt solutions (Fig. 3) reveal that the dimension (hydrodynamic diameter) of the CMC molecules is smaller than 10 nm in

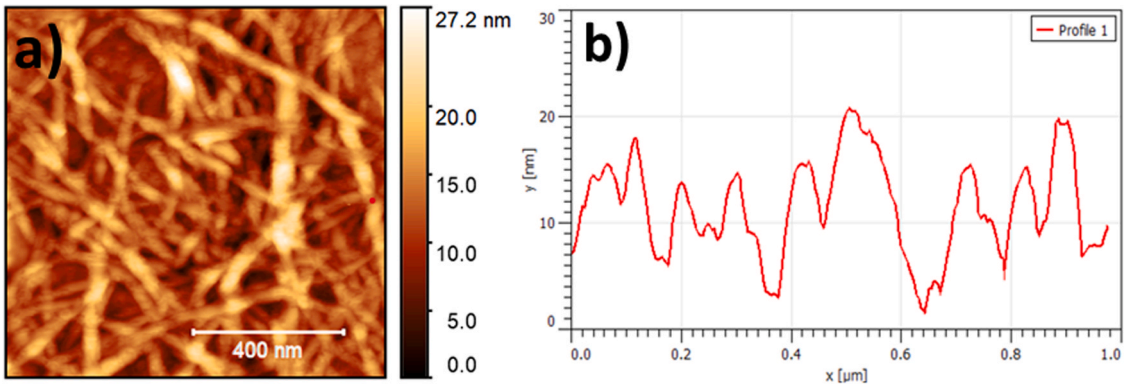


Fig. 1. (a) A representative AFM micrograph of spin-coated CNF film on an SiO_2 coated QCM-D sensor and (b) a typical height profile of CNF model film along a horizontal line.

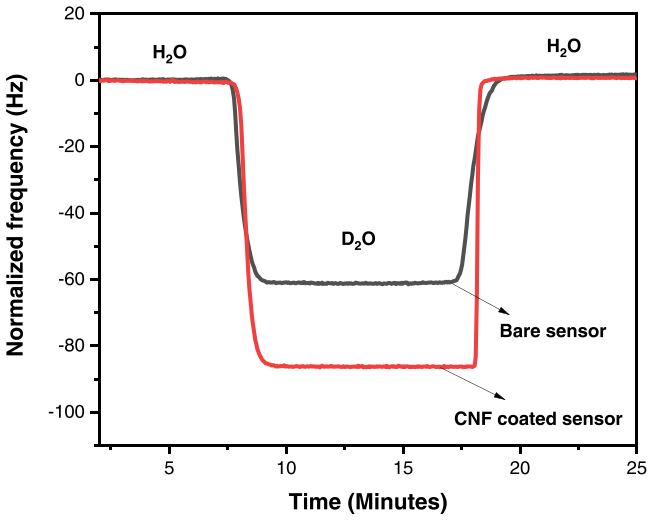


Fig. 2. A representative QCM frequency change of D_2O- H_2O exchange studies on a bare sensor and CNF thin film.

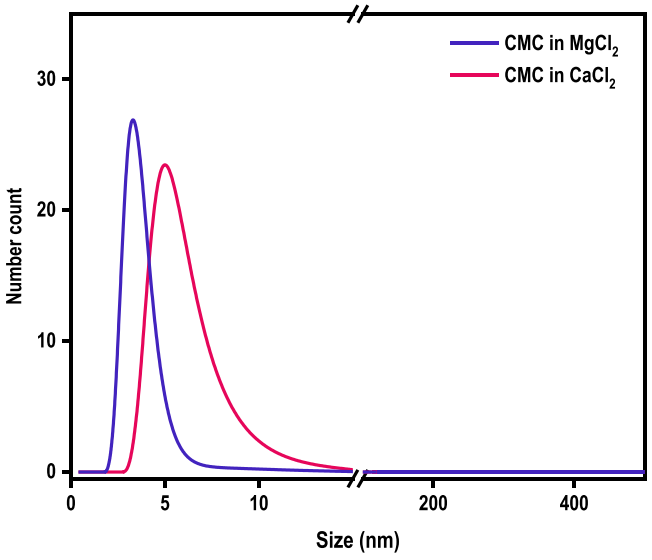


Fig. 3. A representative number-based size distribution of CMC in solutions of 20 mM $CaCl_2$ and 20 mM $MgCl_2$, respectively.

$CaCl_2$ and $MgCl_2$. However, the hydrodynamic diameter of CMCs in the $CaCl_2$ solution (5 nm) is larger than for CMCs in $MgCl_2$ (3.5 nm). The hydrodynamic diameter of CMCs in 20 mM NaCl was also evaluated and found to be 9.7 nm, i.e. larger than that of CMCs in a divalent ionic environment.

3.3. Adsorption studies using QCM-D

Observations made in the solvent exchange studies showed that the cellulose surface undergoes swelling on contact with water. It thus contains high amount of water, which challenges estimations of the amount of CMC adsorbed. Moreover, polyelectrolyte adsorption can also alter the water content in the film [11]. An equilibration step of the CNF films with corresponding salt solutions (20 mM $CaCl_2$ or 20 mM $MgCl_2$) was hence employed prior to each measurement. It was found that it could take up to 1 h 30 min before a plateau in the frequency was attained, indicating that equilibrium in the hydration process had been reached.

An immediate drop in frequency was observed as soon as solutions containing CMC were injected into the flow cell, indicating an increase in the mass at the solid/liquid interface (Fig. 4). Corresponding increase in dissipation also observed in both cases which indicates viscoelastic nature of adsorbed layers. This behaviour was similar to previous reports on the adsorption of CMCs on regenerated cellulose surface [29]. After rinsing with a corresponding salt solution, the frequency shifted to a less negative value, indicating that some of the loosely bound adsorbed chains desorbed from the surface. The results also show that the adsorbed layer had not reached a state of equilibrium after rinsing for 50 min. The sensed mass, calculated by Johannsmann's method prior to and post rinsing, is reported in Table 1 for both salt solutions. The CMC layer adsorbed in the presence of $CaCl_2$ was more stable compared to the CMC layer adsorbed in the presence of $MgCl_2$.

3.4. Adsorption studies on Kraft pulp fibres

The studies undertaken on the adsorption of CMC on model cellulose surfaces revealed that the adsorption of CMC is of an ion-specific nature. In order to evaluate ion-specific adsorption further, the adsorption of CMC on a bulk surface was carried out using commercially available cellulose fibres as the substrate (bleached softwood Kraft pulp fibres). Fig. 5 shows the total charge for CMC-modified and non-modified cellulose fibres, where a larger total charge indicates that the negatively charged CMC has been adsorbed onto the cellulose fibres.

The pulp modified with CMC in $CaCl_2$ and $MgCl_2$ environments showed an increase in total charge content compared to the unmodified pulp, which further shows that there is an attachment of CMC chains on the cellulose surface [13].

The trend observed with an increased total charge and the amount of

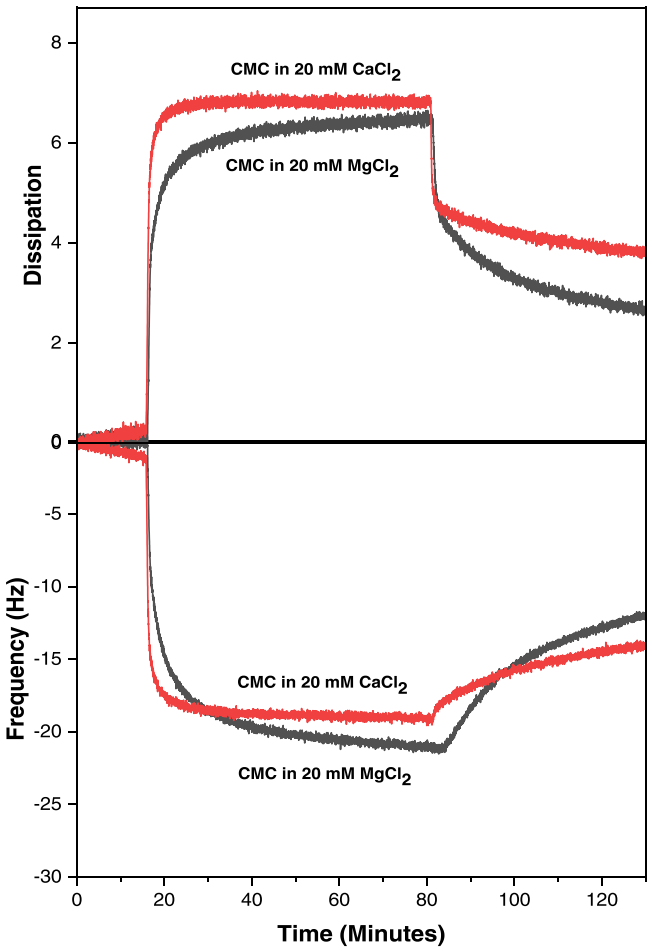


Fig. 4. Changes in frequency and dissipation over time during the adsorption of CMC on CNF films from solutions containing 20 mM $CaCl_2$ and $MgCl_2$ respectively.

CMC attached (Table 2) when calcium ions are present rather than magnesium ions is consistent with the amounts of CMC indicated in the filtrate examined by TOC and polyelectrolyte titration analysis (see Table S1 in Supporting Information). However, compared with results of Laine et al. [28], the increase in total charge obtained in this study is lower. This can be due to the fact that the experiments reported earlier were conducted at higher temperatures and higher salt concentrations, which favour CMC adsorption on cellulose fibres [28]. It should also be noted that the CMC used in this investigation has a low molecular weight and high degree of substitution (DS), which are known to suppress such adsorption [28].

Measurements of surface charge indeed supported previous observations that the amount of CMC adsorbed was greater in the presence of $CaCl_2$ than $MgCl_2$ (Table 3). However, when the total charge measurements and surface charge measurements are compared, it is evident that the contribution made by the surface charge to the total charge is only 15%, so 85% of the charges are located inside the fibre wall. In the present investigation, the percentage increase in surface charge at

Table 1
Amount of CMC adsorbed on CNF calculated using the Johannsmann model [21].

Salt	Sensed mass (mg/m^2)	
	Prior to rinsing	Post rinsing
$MgCl_2$	4.4 ± 0.2	2.8 ± 0.3
$CaCl_2$	4.2 ± 0.4	3.1 ± 0.1

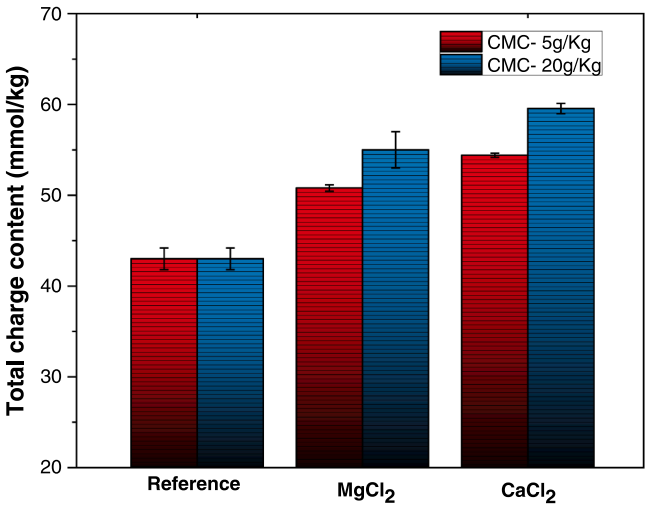


Fig. 5. Total charge of unmodified cellulose fibres and those modified with different amounts of CMC in $CaCl_2$ and $MgCl_2$ environments.

higher loadings of CMC was about 30%. Laine et al. [28] found an increase in the surface charge content relative to the total charge content in excess of 40%. However, their CMC had a larger Mw (280 kDa) compared to the CMC (90 kDa) used here in this study: its smaller dimensions allows a larger amount to penetrate the fibre wall, thereby resulting in a lower surface selectivity. The percentage increase in the surface charge of pulp treated with CMC in the presence of $MgCl_2$ was nevertheless slightly higher than for the pulp treated in the presence of $CaCl_2$. Indeed, according to the data shown in Fig. 5 and Table 2, the amount of adsorbed CMC was greater when a higher CMC concentration was used (about 10% increase in total charge when the concentration of CMC was increased by a factor of four). This, together with the data in Fig. 5, indicates that the adsorption sites available in cellulose pulp are close to saturation at a concentration of 5 g CMC /kg pulp. The information obtained from adsorption studies performed on the commercial pulp and the QCM-D studies showed that CMC adsorbs in considerable amounts in the presence of both Mg^{2+} and Ca^{2+}. However, the amounts adsorbed in $MgCl_2$ were more moderate than those adsorbed in $CaCl_2$. The CMC layer adsorbed from the $CaCl_2$ solution was also more stable compared to that adsorbed from the $MgCl_2$ environment, which also complies with the findings of others [29]. This indicates that an ion-specific mechanism occurs when CMC is adsorbed on cellulose fibre surfaces.

4. Discussion

4.1. Interaction of metal ions with carboxylic groups

The selection of the metal ion has been shown to induce several changes in the interactions that take place between materials containing carboxylate groups (—COO^-), such as gelation and changes to rheological and mechanical properties [1,20,23,33,35] where, for example, the gel strength of polygalactoglucoronate was higher when cross-linked

Table 2
Total charge and amount of CMC attached on modified fibres in the presence of $CaCl_2$ and $MgCl_2$ at two different CMC loadings.

Salt	Total charge content (mmol/g)			Amount of CMC attached (mg/g)	
	CMC (0 g/kg)	CMC (5 g/kg)	CMC (20 g/kg)	CMC (5 g/kg)	CMC (20 g/kg)
$MgCl_2$	43	50.9	55.0	2.0	2.9
$CaCl_2$	43	54.1	56.9	3.1	3.6

Table 3
Surface charge and increase in total charge of the modified fibres.

Salt	Surface charge content mmol/g			Increase in total charge content mmol/g		Percentage of increase in total charge on surface	
	CMC (0 g/kg)	CMC (5 g/kg)	CMC (20 g/kg)	CMC (5 g/kg)	CMC (20 g/kg)	CMC (5 g/kg)	CMC (20 g/kg)
$MgCl_2$	4.7	6.1 ± 0.6	8.5 ± 0.1	7.8	12.0	18.1	31.5
$CaCl_2$	4.7	6.3 ± 0.1	8.8 ± 0.1	11.1	13.9	14.6	29.4

with Ca^{2+} ion than with Mg^{2+} ions. These changes are often assigned to the formation of metal-ligand complexes [20]. The stability of metal-ligand complexes is typically represented by a stability constant, which is logarithm of the first association constant k_1 [17]. Often, there is an insufficient correlation between the stability constant of the metal complex and the property changes observed. For example, Ca^{2+} shows stronger interactions than Mg^{2+} with —COO^- when these groups are located in polyelectrolytes such as alginate or pectin [38,39]. It has been shown, however, [17] that the stability constant of (—COOMg) is higher than that of (—COOCa) complexes; similar observations have been also reported by Lombardo et al. [30]. An unequivocal statement pertaining to ion-induced interactions between cellulose materials due to the formation of metal complexes cannot therefore be made based on the literature. Our findings indicate that the presence of Ca^{2+} enhances CMC adsorption, thereby implying that interactions between CMC chains and the cellulose fibre surface are stronger.

4.2. Specific ionic effects on the adsorption of CMC

It is well known that polymer adsorption is a multifaceted process that involves a polymer solution (liquid phase) and a surface immersed in it, where characteristics of both the solution and the surface can affect the adsorption processes. According to Cohen Stuart et al. [5], adsorption of polyelectrolytes on surfaces with the same charge as the polyelectrolyte is driven by non-electrostatic forces; it has also been suggested that the amount adsorbed increases as the salt concentration increases, and which was later observed experimentally [5,29]. However, comparing the ability of divalent metal ions with monovalent salts to increase the amount adsorbed at the same ionic strength suggests that, apart from obvious electrostatic screening effects, the divalent metal ions contribute positively to the adsorption process. This positive contribution of multivalent ions to adsorption might originate from the structural changes in polymer solutions that are induced by multivalent ions [9,31].

It is suggested here that the effect of divalent ions on the adsorption of polyelectrolytes can be explained by adopting the semi-quantitative model proposed by Benselfelt et al. [3] for the ion-induced assembly of negatively-charged nanofibres. This model takes into account dispersion interactions, ion-ion correlation, metal-ligand complexation and interactions due to changes in the local acidic environment [3].

Two plausible mechanisms that could be involved in ion-induced interactions in CMC adsorptions on cellulose are:

(1) Ion-ion correlations among CMC chains and between CMC chains the cellulose surface induced by the divalent ions.
(2) Dispersion interactions among CMC chains (Fig. 6a) and between CMC chains the cellulose surface induced by the divalent ions (Fig. 6b).

Interactions that occur through ion-ion correlation mechanisms depend on the charge density of the interacting materials and valency of the counter ions. Both the ions used in this study are divalent: the interactions caused by ion-ion correlation should be the same in both cases and therefore cannot be the reason for the difference observed in the amount adsorbed.

The obvious difference between Ca^{2+} and Mg^{2+} is the size of the ions: Ca^{2+} ions are about 30% larger, resulting in their having a higher polarizability [32]. The polarizability of ions has been correlated to dispersion interactions: these are caused by the introduction of local fluctuations in the electron cloud in the ions, which gives rise to the formation of temporary dipoles. The induced dipoles in the electron cloud around the ions can interact with the permanent or introduced dipoles in the polyelectrolyte chains and at the cellulose surfaces which can, in turn, induce interactions among the polyelectrolyte chains and as well as interactions of CMC chains with the cellulose surface. Dispersion interactions are regarded as being the main specific ion effect; it has also been suggested as being the explanation behind the Hofmeister series [34].

The greater polarizability of Ca^{2+} ions means that they can induce stronger dispersion interactions compared to Mg^{2+} ions. The size of the

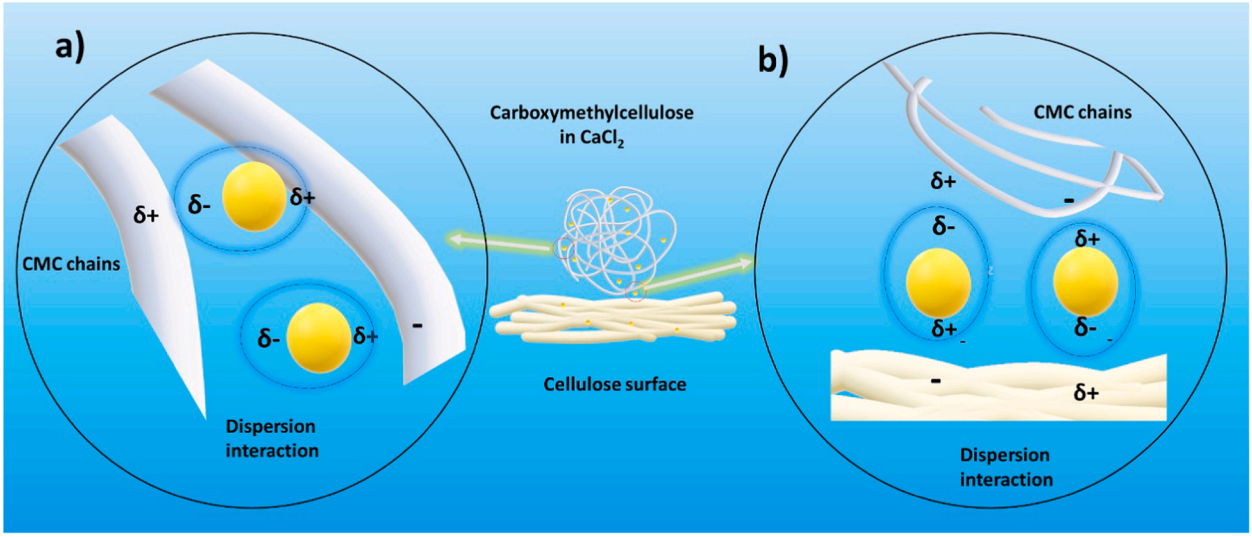


Fig. 6. Dispersion interactions induced by Ca^{2+} ions between (a) CMC chains in solution and (b) CMC chains and a cellulose surface.

CMC was determined using DLS, which showed that in presence of divalent ions the hydrodynamic radius, (R_h) of the CMC has been reduced compared to the hydrodynamic radius of CMC in NaCl solutions of same ionic strength (R_h(CMC-Na) = 9.7 ± 0.3 nm). However, the hydrodynamic radius of of CMC solutions in the presence of Ca^{2+} ions had a tendency to be somewhat larger than hydrodynamic radius in Mg^{2+} solutions (R_h(CMC-Ca) = 5.0 ± 1.0 nm) and (R_h(CMC-Mg) = 3.5 ± 0.5 nm). It has been shown that, unlike Mg^{2+} ions, specifically interacting ions (such as Ca^{2+} and Ba^{2+}) can form interchain cross links between CMC polymer chains, and forms CMC clusters of 20-40 nm in size [36]. Similar Ca^{2+} induced multichain association could be the reason for larger hydrodynamic size. It is also noteworthy that greater interaction of carboxyl groups in the CMC chain could lead to less solvent-polymer interactions, which can favour the adsorption process. However, the difference observed in the R_h of CMC in calcium chloride and magnesium chloride was not remarkably large, which is in agreement with the rheological properties observed by Lopes and Richtering [31]. The difference in R_h is therefore probably not the sole factor for the differences observed when CMC adsorption is compared in presence of Ca^{2+} and Mg^{2+}: increased interaction between CMC and the cellulosic surface through dispersion interactions induced by calcium ions is probably of greater importance. The higher polarizability of calcium ion can cause local enrichment of Ca^{2+} ions close to the surface through dispersion interactions, thereby contributing to bridging between the CMC and the cellulose surface and consequently increasing the amount of CMC adsorbed.

5. Conclusions

The combination of the model experiments using QCM-D and adsorption studies on cellulose pulp fibres revealed that, when compared to Mg^{2+}, the presence of Ca^{2+} enhanced the adsorption of CMC on cellulosic surfaces significantly. This was shown by analyses of the total and surface charges of the cellulose fibres and the remaining CMC in the filtrate after washing of the modified cellulose fibres, as well as the adsorption of CMC on the model studied by QCM-D. The differences observed in the amount of CMC adsorbed could be due to the differences in polarizability of the divalent ions. The higher polarizability of the Ca^{2+} ions introduced CMC with a greater hydrodynamic radius in the presence of calcium chloride solutions than in magnesium chloride solutions. This change in solution behaviour could, at least partly, explain the differences in adsorption behaviour induced by both Ca^{2+} and Mg^{2+}. Furthermore, it can be suggested that the higher polarizability of calcium can cause local enrichment of Ca^{2+} ions close to the surface through dispersion interactions, which can contribute to bridging between CMC and the cellulose surface and thus increase the amount of CMC adsorbed. Despite Mg^{2+} ions being poor adsorption mediators compared to Ca^{2+} they can be used to modulate the adsorption of CMC in an industrial situation. Further investigations into improving the efficiency of Mg^{2+} electrolyte systems should nevertheless be carried out in order to realize the integration of a CMC adsorption step into current pulping mill processes.

CRediT authorship contribution statement

Vishnu Arumughan: Investigation, Analysis, Visualization, Writing - review & editing. **Tiina Nypelö:** Conceptualization Writing - review & editing. **Merima Hasani:** Conceptualization, Writing - review & editing. **Harald Brelid:** Conceptualization, Analysis. **Sverker Albertsson:** Project organization, Review results (before he passed away). **Lars Wågberg:** Conceptualization, Reviewing. **Anette Larsson:** Supervision, Conceptualization Writing - review & editing, Funding acquisition, Project management and editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This project is part of the AvanCell network; it is financed partially by Treesearch, BIOINNOVATION, VINNOVA, Sweden and partially by Södra Foundation for Research, Development and Education, Sweden, both of which are gratefully acknowledged.

We would like to express our heartfelt condolence to Sverker's family for his demise in 2020.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.colsurfa.2021.127006.

References

[1] F.B. Ahmad, P.A. Williams, Effect of salts on the gelatinization and rheological properties of sago starch, J. Agric. Food Chem. 47 (1999) 3359–3366, https://doi.org/10.1021/jf981249r.
[2] S. Ahola, J. Salmi, L.S. Johansson, J. Laine, M. Österberg, Model films from native cellulose nanofibrils. Preparation, swelling, and surface interactions, Biomacromolecules 9 (2008) 1273–1282, https://doi.org/10.1021/bm701317k.
[3] T. Benselfelt, M. Nordenström, M.M. Hamedi, L. Wågberg, Ion-induced assemblies of highly anisotropic nanoparticles are governed by ion-ion correlation and specific ion effects, Nanoscale 11 (2019) 3514–3520, https://doi.org/10.1039/c8nr10175b.
[4] N. Butchosa, Q. Zhou, Water redispersible cellulose nanofibrils adsorbed with carboxymethyl cellulose, Cellulose 21 (6) (2014) 4349–4358, https://doi.org/10.1007/s10570-014-0452-7.
[5] M.A. Cohen Stuart, G.J. Fleer, J.M.H.M. Scheutjens, Displacement of polymers. I. Theory. Segmental adsorption energy from polymer desorption in binary solvents, J. Colloid Interface Sci. 97 (1984) 515–525, https://doi.org/10.1016/0021-9797(84)90323-0.
[7] V.S.J. Craig, M. Plunkett, Determination of coupled solvent mass in quartz crystal microbalance measurements using deuterated solvents, J. Colloid Interface Sci. 262 (2003) 126–129, https://doi.org/10.1016/S0021-9797(03)00210-8.
[8] N. Das, S. Bose, D. Biswas, Effect of magnesium-salts on hydrogen peroxide bleaching of non-wood pulps, Bangladesh J. Sci. Ind. Res. 51 (4) (2016) 291–296, https://doi.org/10.3329/bjsir.v51i4.30449.
[9] W.M. de Vos, S. Lindhoud, Overcharging and charge inversion: Finding the correct explanation(s), Adv. Colloid Interface Sci. 274 (2019), 102040, https://doi.org/10.1016/j.cis.2019.102040.
[10] P. Ekevåg, T. Lindström, G. Gellerstedt, M.E. Lindström, Addition of carboxymethylcellulose to the kraft cook, Nord. Pulp Pap. Res. J. 19 (2004) 200–207, https://doi.org/10.3183/npprj-2004-19-02-p200-207.
[11] L.E. Enarsson, L. Wågberg, Polyelectrolyte adsorption on thin cellulose films studied with reflectometry and quartz crystal microgravimetry with dissipation, Biomacromolecules 10 (2009) 134–141, https://doi.org/10.1021/bm8010193.
[12] C. Fechter, T. Heinze, Influence of wood pulp quality on the structure of carboxymethyl cellulose, J. Appl. Polym. Sci. 136 (2019) 47862, https://doi.org/10.1002/app.47862.
[13] L. Fras Zemljič, P. Stenius, J. Laine, K. Stana-Kleinschek, Topochemical modification of cotton fibres with carboxymethyl cellulose, Cellulose 15 (2008) 315–321, https://doi.org/10.1007/s10570-007-9175-3.
[14] A. Giglio, Calcite Scale Formation in the Green Liquor Handling System of the Kraft Chemical Recovery Process, 2018.
[15] G.J Fleer, Polymers at interfaces, in: G.J. Fleer, M.A. Cohen Stuart, J.M.H. M. Scheutjens, T. Cosgrove, B. Vincent (Eds.), Polymer International, Chapman and Hall, London, 1995. ISBN 0-412-58160-4.
[16] P.T. Hammond, Engineering materials layer-by-layer: challenges and opportunities in multilayer assembly, AIChE J. 57 (2011) 2928–2940, https://doi.org/10.1002/aic.12769.
[17] R.D. Hancock, F. Marsicano, Parametric correlation of formation constants in aqueous solution. 2. Ligands with large donor atoms, Inorg. Chem. 19 (1980) 2709–2714, https://doi.org/10.1021/ic50211a045.
[18] T. Heinze, T. Liebert, P. Klüfers, F. Meister, Carboxymethylation of cellulose in unconventional media, Cellulose 6 (1999) 153–165, https://doi.org/10.1023/A:1009271427760.
[19] E. Horvath, The effects of cellulosic fibre charges on polyelectrolyte adsorption and fibre-fibre interactions, Diss (2006), 2006.
[20] U.T.D. Huynh, A. Lerbret, F. Neiers, O. Chambin, A. Assifaoui, Binding of divalent cations to polygalacturonate: a mechanism driven by the hydration water, J. Phys. Chem. B 120 (2016) 1021–1032, https://doi.org/10.1021/acs.jpcb.5b11010.

[21] D. Johannsmann, K. Mathauer, G. Wegner, W. Knoll, Viscoelastic properties of thin films probed with a quartz-crystal resonator, Phys. Rev. B, Condens. Matter 46 (1992) 7808–7815, https://doi.org/10.1103/PhysRevB.46.7808.
[22] R. Kargl, T. Mohan, M. Bračč, M. Kulterer, A. Doliška, K. Stana-Kleinschek, V. Ribitsch, Adsorption of carboxymethyl cellulose on polymer surfaces: evidence of a specific interaction with cellulose, Langmuir 28 (2012) 11440–11447, https://doi.org/10.1021/la302110a.
[23] P. Khanjani, H. Kosonen, M. Ristolainen, P. Virtanen, T. Vuorinen, Time-triggered calcium ion bridging in preparation of films of oxidized microfibrillated cellulose and pulp, Carbohydr. Polym. 218 (2019) 63–67, https://doi.org/10.1007/s10570-019-02417-w.
[24] J.D. Kittle, X. Du, F. Jiang, C. Qian, T. Heinze, M. Roman, A.R. Esker, Equilibrium water contents of cellulose films determined via solvent exchange and quartz crystal microbalance with dissipation monitoring, Biomacromolecules 12 (2011) 2881–2887, https://doi.org/10.1021/bm200352q.
[25] T. Köhnke, H. Brelid, G. Westman, Adsorption of arabinoxylan on cellulosic surfaces: influence of degree of substitution and substitution pattern on adsorption characteristics, Biomacromolecules 12 (2011) 2633–2641, https://doi.org/10.1007/s10570-009-9341-x.
[26] E. Kontturi, M. Mitikka-Eklund, T. Vuorinen, Amorphous characteristics of an ultrathin cellulose film, Biomacromolecules 12 (2011) 770–777, https://doi.org/10.15376/biores.3.1.34-45.
[27] J. Laine, T. Lindström, G.G. Nordmark, G. Risinger, Studies on topochemical modification of cellulosic fibres Part 2, Nord. Pulp Pap. Res. J. 17 (1) (2002) 50–56.
[28] J. Laine, T. Lindström, G.G. Nordmark, G. Risinger, Studies on topochemical modification of cellulosic fibres, Nord. Pulp Pap. Res. J. 15 (2000) 520–526, https://doi.org/10.3183/NPPRJ-2000-15-05-p520-526.
[29] Z. Liu, H. Choi, P. Gatenholm, A.R. Esker, Quartz crystal microbalance with dissipation monitoring and surface plasmon resonance studies of carboxymethyl cellulose adsorption onto regenerated cellulose surfaces, Langmuir: ACS J. Surf. Colloids 27 (2011) 8718–8728, https://doi.org/10.1021/la200628a.
[30] S. Lombardo, A. Gençer, C. Schütz, J. Van Rie, S. Eyley, W. Thielemans, Thermodynamic study of ion-driven aggregation of cellulose nanocrystals, Biomacromolecules 20 (2019) 3181–3190, https://doi.org/10.1021/acs.biomac.9b00755.
[31] C.G. Lopez, W. Richtering, Influence of divalent counterions on the solution rheology and supramolecular aggregation of carboxymethyl cellulose, Cellulose 26 (2019) 1517–1534, https://doi.org/10.1007/s10570-018-2158-8.
[32] J. Mitroy, M.S. Safronova, C.W. Clark, Theory and applications of atomic and ionic polarizabilities, J. Phys. B At. Mol. Opt. Phys. 43 (2010), 202001, https://doi.org/10.1088/0953-4075/43/20/202001.
[33] M.A. Montoro, F.M. Francisca, Effect of ion type and concentration on rheological properties of natural sodium bentonite dispersions at low shear rates, Appl. Clay Sci. 178 (2019), 105132, https://doi.org/10.1016/j.clay.2019.105132.
[34] B.W. Ninham, P. Lo Nostro, Molecular forces and self assembly:in colloid, nano sciences and biology, Mol. Forces Self Assem. Colloid, Nano Sci. Biol. (2010), https://doi.org/10.1017/CBO9780511811531.
[35] F.O. Obiweluozor, A. Ghavaminejad, S. Hashmi, M. Vatankhah-Varnoosfaderani, F. J. Stadler, A NIPAM-Zwitterion copolymer: rheological interpretation of the specific ion effect on the LCST, Macromol. Chem. Phys. 215 (2014) 1077–1091, https://doi.org/10.1002/macp.201300778.
[36] W.N. Sharratt, R. O'Connell, S.E. Rogers, C.G. Lopez, J.T. Cabral, Conformation and phase behaviour of sodium carboxymethyl cellulose in the presence of mono and divalent salts, Macromolecules 53 (4) (2020) 1451–1463, https://doi.org/10.1021/acs.macromol.9b02228.
[37] J.V. Swintosky, L. Kennon, A note on the preparation of powdered carboxymethyl-cellulose and linseed acids, J. Am. Pharm. Assoc. 42 (8) (1953) 505, https://doi.org/10.1002/jps.3030420815.
[38] J.F. Thibault, M. Rinaudo, Interactions of mono and divalent counterions with alkali and enzyme-deesterified pectins in salt-free solutions, Biopolymers 24 (1985) 2131–2143, https://doi.org/10.1002/bip.360241109.
[39] D. Thom, G.T. Grant, E.R. Morris, D.A. Rees, Characterisation of cation binding and gelation of polyuronates by circular dichroism, Carbohydr. Res. 100 (1982) 29–42, https://doi.org/10.1016/S0008-6215(00)81023-X.
[40] A. Villares, C. Moreau, A. Dammak, I. Capron, B. Cathala, Kinetic aspects of the adsorption of xyloglucan onto cellulose nanocrystals, Soft Matter 11 (2015) 6472–6481, https://doi.org/10.1039/c5sm01413a.
[41] L. Wågberg, M. Bjorklund, Adsorption of cationic potato starch on cellulosic fibres, Nord. Pulp Pap. Res. J. (2007), https://doi.org/10.3183/npprj-1993-08-04-p399-404.
[42] L. Wågberg, J. Erlandsson, The use of layer-by-layer self-assembly and nanocellulose to prepare advanced functional materials, Adv. Mater. (2020), 2001474, https://doi.org/10.1002/adma.202001474.
[43] L. Winter, L. Wågberg, L. Ödberg, T. Lindström, Polyelectrolytes adsorbed on the surface of cellulosic materials, J. Colloid Interface Sci. 111 (2) (1986) 537–543, https://doi.org/10.1016/0021-9797(86)90057-3.
[44] X. Xu, D. Mastropietro, M. Ruths, M. Tirrell, J. Yu, Ion-specific effects of divalent ions on the structure of polyelectrolyte brushes, Langmuir 35 (2019) 15564–15572, https://doi.org/10.1021/acs.langmuir.9b01984.
[45] A. de Keizer, et al., Adsorption mechanisms of carboxymethyl cellulose on mineral surfaces, Langmuir 14 (2002) 3825–3839, https://doi.org/10.1021/la9800046.